III.F.2 A Low-Cost Process for the Synthesis of Nanosize Yttria-Stabilized Zirconia (YSZ) by Molecular Decomposition

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Objectives

- To synthesize Y-BaZrO$_3$, Y-Na$_2$ZrO$_3$, and Y-CaZrO$_3$ starting with commercial-grade powders of precursors.
- To synthesize and characterize the nanosize YSZ formed. Characterization includes (a) surface area, (b) particle size, (c) agglomerate size, and (d) composition.
- To sinter YSZ discs and bars made from the nanosize YSZ powder, and characterize the sintered samples. Characterization includes (a) density, (b) grain size, and (c) conductivity.
- To conduct a preliminary design of a process for the synthesis of nanosize YSZ powder.

Approach

- Mix _macrosize_, inexpensive Y$_2$O$_3$, ZrO$_2$, and NaOH (or Ba(NO$_3$)$_2$) powders in the desired proportions to form Y-doped Na$_2$ZrO$_3$ (or Y-doped BaZrO$_3$).
- Calcine at ~1100°C in air to form Y-doped Na$_2$ZrO$_3$ (or Y-doped BaZrO$_3$). The reactions are as follows:

  $$2NaOH + x/2Y_2O_3 + (1-x)ZrO_2 \rightarrow Na_2Zr_{(1-x)}Y_xO_{(3-x/2)} + H_2O$$
  or
  $$Ba(NO_3)_2 + x/2Y_2O_3 + (1-x)ZrO_2 \rightarrow BaY_xZr_{(1-x)}O_{(3-x/2)} + N_2 + 5/2O_2$$

  In what follows, we will denote Na$_2$Zr$_{(1-x)}$Y$_x$O$_{(3-x/2)}$ by Y-Na$_2$ZrO$_3$ and BaY$_x$Zr$_{(1-x)}$O$_{(3-x/2)}$ by Y-BaZrO$_3$.

- Leach in water to form and dissolve away NaOH by the following reaction:

  $$Y\text{-}Na_2ZrO_3 + (n+1)H_2O \rightarrow Y\text{-}ZrO_2 + 2NaOH + nH_2O$$

  The NaOH formed is dissolved in water, and Y-ZrO$_2$ (YSZ) is a nanosize residue.
  or
  Leach in HNO$_3$ to form and dissolve Ba(NO$_3$)$_2$ by the following reaction:

  $$Y\text{-}BaZrO_3 + 2HNO_3 + nH_2O \rightarrow Y\text{-}ZrO_2 + Ba(NO_3)_2 + (n+1)H_2O$$

  The Ba(NO$_3$)$_2$ formed is dissolved in water, and Y-ZrO$_2$ (YSZ) is a nanosize residue.

- Dry the NaOH (or Ba(NO$_3$)$_2$) solution, and recycle NaOH (or Ba(NO$_3$)$_2$).

Accomplishments

- From the two selected precursors, namely Y-doped BaZrO$_3$ and Y-doped Na$_2$ZrO$_3$, selection of Y-doped Na$_2$ZrO$_3$ was made for the synthesis of nanosize (or fine) YSZ. This was based on the potential cost of the precursor, the need to use only water for leaching, and the short time required for the process.

- For the synthesis of calcia-stabilized zirconia (CSZ), which has the potential for use in place of YSZ in the anode of the SOFC, Ca-doped Na_2ZrO_3 was demonstrated as a suitable precursor.

- Synthesis of Y-doped Na_2ZrO_3 and Ca-doped Na_2ZrO_3 was achieved using a conventional calcination process. The corresponding surface area was ~1 to 2 m^2/g.

- By leaching with water, nanosize (very fine) YSZ and CSZ powders were synthesized. The corresponding surface area was ~65 m^2/g. This demonstrates the molecular decomposition (MD) concept, namely macroscopic precursor → leaching → very fine (nanosize) product.

- Anode-supported cells, with YSZ and CSZ made by the MD process, were successfully made by a conventional pressing and sintering process.

- A single cell (Sr-doped $LaMnO_3$ (LSM) + YSZ cathode) was tested at 800°C with H_2/air, with maximum power density of ~1.2 W/cm^2.

- Preliminary cost analysis, based on materials cost only, showed that the cost of YSZ powder made by the MD process should be considerably lower than that of YSZ powder made by either chemical co-precipitation or combustion synthesis.

Future Directions

The funded project has been completed, and no more work is planned. However, the following work is necessary for full evaluation of the process.

- Fabricate and test large-area (100 cm^2) cells in short stacks to evaluate performance.

- Design, construct and demonstrate a lab-scale reactor for the synthesis of CSZ and YSZ by molecular decomposition.

- Conduct a detailed cost analysis of the process.

Introduction

In order to facilitate the fabrication of solid oxide fuel cells by ceramic processing methods, it is necessary to use high-quality powders that are fine and not agglomerated. If the powders are fine (nanosize) and also de-agglomerated, processing temperature can be lowered, thus lowering the cost of energy and also minimizing materials interactions. One of the important materials is yttria-stabilized zirconia, or YSZ. At the present, commercially available powders of high quality sell for ~$100/kg, which is too expensive to be practical. One of the main reasons for the high cost is the cost of water-soluble salts used in the conventional fabrication process. This process is based on *molecular synthesis*, which involves an atom-by-atom or a molecule-by-molecule addition to a growing particle.

The University of Utah has invented a novel process for the synthesis of nanosize powders based on the concept of *molecular decomposition* (MD), which is a radical departure from the traditional approach. This approach has numerous technological advantages over the traditional approaches. This method is based on forming an insoluble but reactive precursor which has a fugitive constituent along with the desired constituent. The precursor synthesis does not require expensive water-soluble salts, but can use inexpensive oxides, carbonates, hydroxides, and the like.

Approach

The basic premise of the process of MD is that by decomposing a larger molecule (or structure) and leaching away fugitive constituents, fragments of the remaining constituents are formed at the atomic or nano level. These fragments then arrange themselves in the most stable structure so as to minimize the net free energy. For the process to work, the following conditions must be satisfied. (1) The precursor must contain the desired constituents of the final product and a fugitive constituent, in a chemically combined form. (2) The precursor must be insoluble in the liquid reagent used, but must react with it. (3) The fugitive constituent must form a soluble compound upon reacting with the reagent. (4) The final product
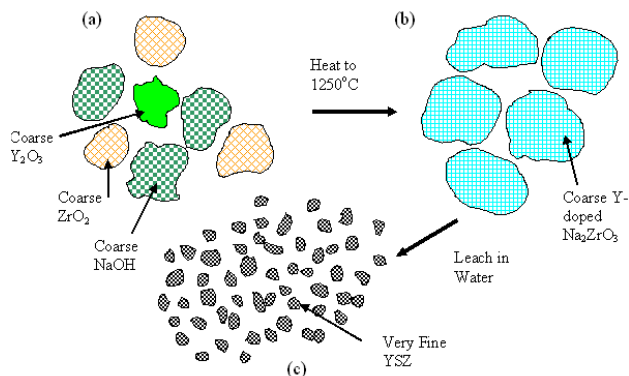
Figure 1. A schematic of the MD process: (a) Mixing of raw materials: Y_2O_3, ZrO_2, and NaOH, all of particle sizes in the micron to tens of microns range. (b) Calcination to form $Y-Na_2ZrO_3$ of several tens of microns in size. (c) Leaching in water to form nanosize YSZ.

must neither react with the reagent, nor dissolve in it. This prevents the occurrence of particle growth by dissolution-re-precipitation (Ostwald ripening).

The approach is described below by way of an example for the formation of nanosize ZrO_2 (n-ZrO_2). (1) A possible precursor is Na_2ZrO_3, which can be formed by reacting macrosize NaOH and macrosize ZrO_2, both of which are inexpensive. Na_2O is the fugitive constituent. (2) Na_2ZrO_3 reacts with water (reagent), but does not dissolve in it. (3) The fugitive constituent reacts with water to form NaOH, which is readily soluble in water. (4) The final product is n-ZrO_2, which does not react (although there is some tendency to form hydroxides) or dissolve in water. For the synthesis of YSZ, the stabilizer Y_2O_3 can be incorporated into the precursor. Alternative precursors and reagents can be used to obtain n-ZrO_2__for example, $BaZrO_3$ and HNO_3.

Results

Figure 1 shows a schematic of the MD process, wherein the precursor can be formed using inexpensive raw materials of large particle sizes (well into the microns or several tens of microns). Once a precursor is formed and reacted with a suitable reagent, the product phase forms fragments at the nanosize level. This method was to make nanosize powders of YSZ and CSZ. The precursors used were Y-doped Na_2ZrO_3 and Ca-doped

Figure 2. A bright field TEM image of nanosize YSZ formed by the MD process. The crystallite size is ~5 nm. The agglomerate size in this TEM image is about 50 to 200 nm. The agglomerates are soft and can be broken with ease, down to a few tens of nm.

Na_2ZrO_3. Figure 2 is a transmission electron micrograph (TEM) bright field image of nanosize YSZ formed by MD. The precursor specific surface area was about 1 to 2 m^2/g. However, the specific surface area of the nanosize YSZ was about 67 m^2/g. The actual surface area should be larger. However, the particles were agglomerated (to form clusters of 50 to 100 nm in size, still in the nano range). X-ray diffraction (XRD) using $CuK\alpha$ radiation (Scherrer formula) showed that the crystallite size is about 3 to 4 nm. The YSZ powder, once properly ball-milled, could be readily sintered to form full dense parts. Figure 3 shows a scanning electron micrograph (SEM) of a sintered sample of YSZ made by MD. Note that the microstructure is equiaxed and that there is negligible porosity. While the nanosize powder made by this process can be used to make dense parts, its principal anticipated use is in the anode support of an anode-supported solid oxide fuel cell (SOFC). Cells were made using n-YSZ made
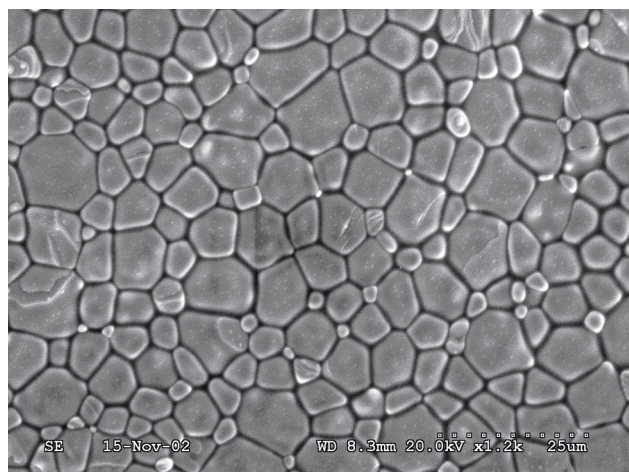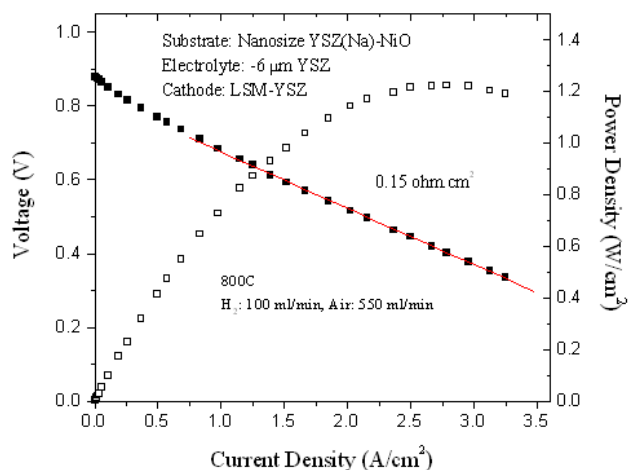
Figure 3. An SEM micrograph of a sintered sample of YSZ made by the MD process. The sample was sintered at 1400°C.

Figure 4. Voltage and power density vs. current density plots for the cell made using YSZ made by the MD process in the anode. In this initial trial, there were a few pinholes in the YSZ film (which was actually made using co-precipitated powder from a commercial source). As such, the open circuit voltage (OCV) is lower than had there been no pinholes. Nevertheless, it can be seen that the cell area specific resistance is quite low (~0.15 Ωcm^2 at 800°C). The corresponding maximum power density is ~1.2 W/cm^2. Had there been no pinholes and the OCV had been ~1.15 V, the maximum power density would have been ~1.9 W/cm^2.

during the course of this project, and cells were tested using hydrogen as fuel and air as oxidant. Figure 4 shows the performance curves for a cell. Note that power density of ~1.2 W/cm^2 was achieved at 800°C. A preliminary cost analysis was performed. It showed that powders made by MD should be less expensive than those made by chemical co-precipitation. The projected cost was less than $10/kg for large batches. Cells were also made using CSZ powder made by MD.

Conclusions

The principal objective of the work was to demonstrate the synthesis and densification characteristics of very fine (nanosize) YSZ made by novel molecular decomposition, a potentially low-cost process. This principal objective was achieved.

In addition to the stated objective of developing very fine YSZ powders by the MD process, other significant results were obtained. These included the fabrication and testing of an anode-supported button cell using YSZ and CSZ made by the MD process as a constituent in the anode. At 800°C, the maximum power density of the cell with MD-YSZ in the anode was about 1.2 W/cm^2. The other significant achievement was the synthesis of calcia-stabilized

zirconia (CSZ) by the MD process. The potential use of CSZ in the anode support is expected to have a beneficial effect of further lowering the cost.

FY 2004 Publications/Presentations

1. "Synthesis of Nanosize Oxide Powders by Molecular Decomposition", by Anil V. Virkar, Invited talk presented at CHEMCON-2003, Bhubaneswar, India, December 2003.

Special Recognitions & Awards

1. Anil V. Virkar received the 'Alkyl Amines Distinguished Speaker Award' of the Indian Institute of Chemical Engineers, December 2003.